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M. Ohkubo, M. Ukibe, N. Saito, A. Kushino, S. Ichimura, and S. Friedrich

***Abstract*— We are developing The spatial uniformity of superconducting tunnel junction detectors with a size of 200 µm is improved by increasing the Al thickness of the Nb/Al proximitized electrodes in an energy range of 5 – 10 keV. which is in the same order as an acceleration energy in time-of-flight mass spectroscopy (TOF-MS). It has been confirmed in TOF experiments with Ta ions and Ta clusters that the proximitized junction detectors clearly separate different ionic states and multi-hit events in impact energy spectra, and moreover can reveal a difference in ion species or ion-surface collision dynamics. However, a better spatial uniformity is not always good for TOF-MS, because a detector with the thicker Al layers has a lower superconducting energy gap, which results in improper detector operation because of a temperature rise due to heat radiation.**

***Index Terms*—Mass spectrometry, particle detectors, super-conductor-insulator-superconductor devices, superconducting radiation detectors**

I. Introduction

CRYOGENIC detectors for ions accelerated by a static electric field in time-of-flight mass spectrometry (TOF-MS) have an unconventional performance of the simultaneous measurement of ion arrival time and impact energy. This performance enables the determination of mass-charge ratio (*m/z*) and the discrimination of different ionic states [1]-[2]. Furthermore, an ion detection efficiency of the cryogenic detectors is expected to be independent on mass up to a few MDa, since they detect non-equilibrium phonons or a temperature rise produced by a single ion-impact instead of a secondary electron emission that occurs in conventional microchannel plate (MCP) detectors. A flat detection efficiency in a wide mass range is important in measuring the real mass-distribution of proteins, DNA, or large polymers, and in calibrating the MCP detectors concerning the dependence of the detection efficiency on mass or ion species.

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Superconducting tunnel junction (STJ) detectors have a faster time resolution of a few 100 ns, which is advantageous for a high mass resolution, than about 1 µs of calorimetric detectors. However, in order for the STJ detectors to replace those with secondary ion multiplication or post-acceleration, an issue is to improve effective detection area. One of the practical solutions is to built the array of hundreds of STJ elements with a size of 100 – 200 µm.

It is known that the STJ detectors with these detector sizes perform well for the energy deposition by photons in a range of less than about 1 keV [3], but the spatial non-uniformity becomes serious in an energy range more than about 5 keV [4]. That high energy range is comparable to ion energies in TOF-MS experiments. The spatial non- uniformity, which means that the pulse height of detector output depends on ion impact site, results in spectral broadening in impact energy measurement. A large spectral broadening makes the ionic state discrimination impossible. In this study, two kinds of single-element STJ detectors with different spatial profiles are compared in TOF-MS experiments with a Ta cluster ion source. The Ta clusters have series mass values in an interval of 180.95 Da with a negligible isotope. A mass range of the Ta ion source can be up to 1 MDa, but normally up to 100 kDa. It is, therefore, an ideal ion source to study such detector performance as the charge discrimination, the mass resolution, *etc*.

II. Experiment

A. STJ ion detectors

Niobium-based STJ detectors were fabricated by conventional photolithographic techniques. The 200µm-square tunnel junctions has a so-called proximized layer-structure of Nb(200nm)/Al/AlO_x/Al/Nb(100nm) on Si substrates. The Al layer thicknesses on both sides of the AlO_x barrier are equal. We have studied two detectors with different Al layer thicknesses of 50 and 70 nm. For the ion detection, a SiO_2 insulating layer that normally covers the entire surface of the tunnel junctions was removed by a selective ion etching technique so that ions hit the top superconducting electrodes directly. It has been experimentally confirmed by a direct imaging method using photoabsorption of synchrtron radiation at 6 keV that the spatial profile depends on the thickness of the Al layers. The measured spatial nonuniformity of the detector output was 20% at 50nm and 4% at 70nm [5].

B. TOF experiments

The TOF experiments were performed in a linear mode with an acceleration voltage of 8.33 kV. The metal cluster ion source generated Ta ions and Ta cluster ions in a mass range less than 100 kDa. In the linear mode, it was difficult to separate the clusters, of which a mass interval is 180.95 Da, in a mass range more than 10 kDa because of a limitation of ion optics. In this study, therefore, we have concentrated on a mass range less than 2 kDa. The detail of the cluster TOF equipment was published elsewhere [6].

The STJ detectors cooled by a ^{3}He refrigerator with a base temperature of 0.33 K were set at the end of a flight tube with a length of about 1.9 m. To avoid a large heat radiation from room temperature, a collimator with a diameter of 1.5 mm was placed on the cold stage at 4 K. The real temperature of the junctions were estimated at about 1.3 K from a subgap-current increase. The output pulses were read out by a custom-made current-sensitive preamplifier with dc voltage bias [7] and such conventional energy and timing electronics as a shaping amplifier and a timing single-channel analyzer, and then the ion impact energy and time-of-flight values were recorded.

The current-sensitive amplifier is advantageous to TOF-MS compared with charge-sensitive preamplifiers, because the output pulses directly reflect the detector response to ion impacts. The output pulses in present experiments have a rise time of a few 100 ns and a fall time of 2-3 µs, which are more than one order of magnitude faster than those of charge-sensitive preamplifiers. Therefore, the current- sensitive preamplifier may accept a large number of ion hit events. We plan to make the rise time faster without instability to improve the mass resolution.

III. Results and Discussion

An example of mass spectra recorded with the STJ detector with an Al thickness of 50 nm is shown in Fig. 1. Most of the observed peaks have an interval of the Ta atom mass, 180.95, on the *m/z* axis, and the univalent clusters up to 11 atoms are clearly separated. The small peaks, which are labeled by 13, 15, 17, and 19, are assigned to the bivalent clusters. The bivalent clusters are stable only in cluster sizes more than 13 atoms. Small bivalent clusters break with coulomb explosion.

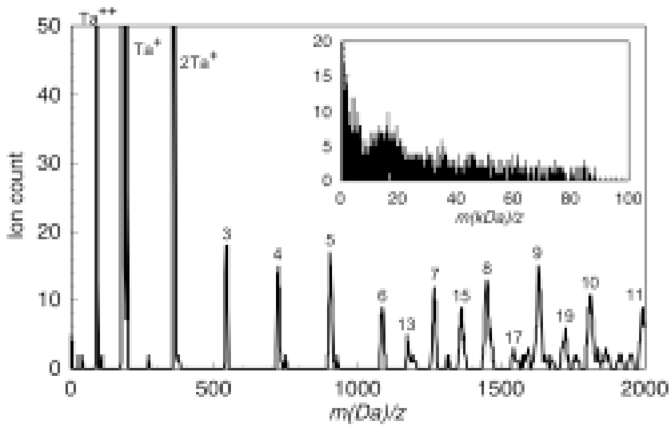

Fig.1. Mass spectra of Ta clusters. The numbers of Ta atoms contained in the clusters are shown. The mass interval is a Ta mass of 180.95. The small peaks labeled by 13, 15, 17, and 19 are assigned to the bivalent clusters.

The Ta^{++} peak was used for evaluating the time resolution of the STJ detector. The peak width of the Ta^{++} ions measured by MCP was 25 ns in full width at half maximum (FWHM). If we assume that this value represents a fluctuation in the ion source, the acceleration, and the readout electronics, the best intrinsic time resolution of the STJ detector is 93 ns. The corresponding peak width for the Ta^{++} ions in the mass spectrum is 0.75 Da, which may be enough to separate a proton mass.

In the Ta clusters, it is possible to discriminate between the univalent ions and the bivalent ions only on mass spectra, since the *m/z* values divided by 180.95 are unequal to integers for bivalent ions. However, when we measure unknown ions, the ionic-state discrimination only on mass spectra is difficult. In this case, the charge discrimination is possible on scatter plots of impact energy vs. time-of-flight, as shown in Fig. 2, which magnifies a part of Ta^+ and Ta^{++} ions in the detector with the 50nm-thick Al layers. Each event is plotted by a dot on a position according to the *x* and *y* axes. In this plot, three groups of the Ta^{++} ions, the Ta^+ ions, and the double hits of the Ta^+ ions are distinguishable. The Ta^{++} group is well separated on both *x* and *y* axes. On the other hand, the Ta^+ double-hit group is on the same vertical line as the Ta^+ group.

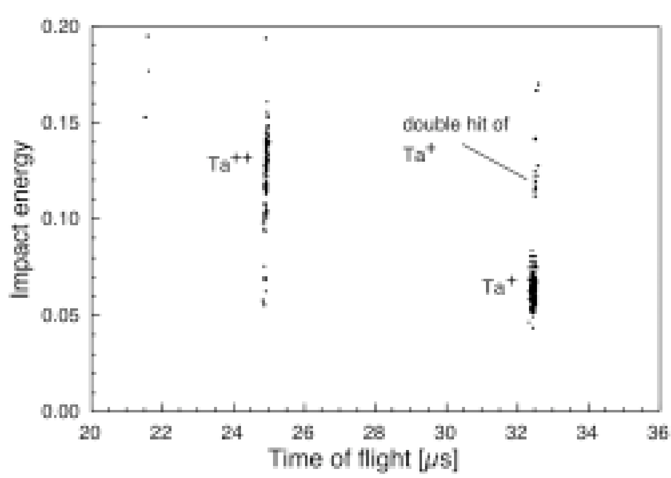

Fig. 2. Scatter plot of impact energy vs. time-of-flight for univalent and bivalent Ta ions.

The performance of the STJ detectors on the impact energy measurement is examined by plotting the ion count yield as a function of the detected impact energy. Fig. 3 shows the impact energy spectra for the detector with the 50nm-thick Al layers. Three time-gates were employed. The spectrum labeled by all events was collected without the time gates. The Ta^{+} spectrum was collected with a time gate at 32.5 μs to record only the Ta^{+} events. For the Ta^{++} spectrum, a time gate was set at 25 μs.

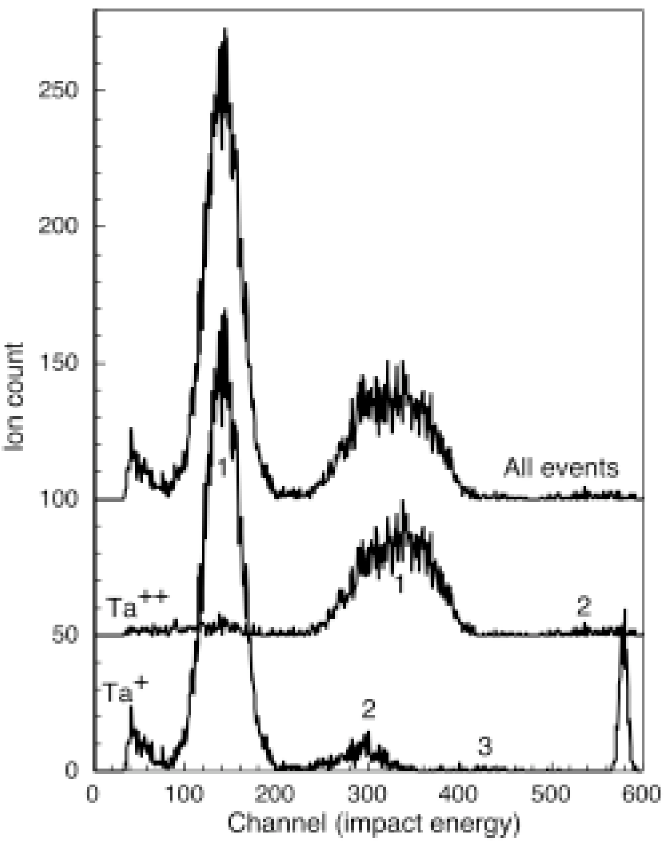

Fig.3. Impact energy spectra for all events, Ta^{++}, and Ta^{+} with different time-gates in the STJ detector with the 50nm-thick Al layers. Multi-hit events are indicated by the numbers. The pulser peak at 580 ch. represents a noise of the readout electronics.

There are two main peaks in the spectrum without the time gates. In consideration of the spectra with the time gates in Fig. 3, two peaks are assigned to the single Ta^{+} events at 140 ch. and the single Ta^{++} events at 330 ch. In the Ta^{+} spectrum, the small peak at 290 ch. has double energy of the single Ta^{+} peak so that it is identified as the Ta^{+} double-hit events. The double Ta^{+} events and single Ta^{++} events should deposit the same energy of 16.7 keV, when we ignore secondary electron, secondary ion, and photon emission. However, the peak position of the single Ta^{++} events is considerably higher than that of the double Ta^{+} events. The single hit events deposit the entire energy at one localized site, while the double hit events deposit it at two separate positions. Since the spatial nonuniformity is 20%, it is reasonable that two impacts at different sites produce a lower response. However, when we compare the single hit events, the peak position of 330 ch. for the single Ta^{++} events is apparently higher than double of 141 ch. of the single Ta^{+} events. The detector responsivity as a function of deposited energy is a complex function, as reported in ref. [8], but in the present energy range the responsivity monotonically decreases as the deposited energy increases. Therefore, it is obvious that the energy deposition of the Ta^{++} ions is more than double of that of the Ta^{+} ions. The above-mentioned results are possibly related to secondary particle emission. Because the projected ranges of the Ta^{+} and Ta^{++} ions in Nb are 40 and 60 Å, respectively, it is expected that the numbers of the secondary particles are different. The deposited fraction of the ion kinetic energy of the Ta^{++} events should be higher than that of the Ta^{+} events. Full understanding about these phenomena requires additional investigation.

The Ta event peaks in Fig. 3 have FWHM values between 45 and 94 ch., which are larger than the pulser peak width of 10 ch. The peak broadening is more than that expected from the pulser width and the spatial nonuniformity. The STJ detectors may provide additional information about ion-surface collision dynamics at low energy.

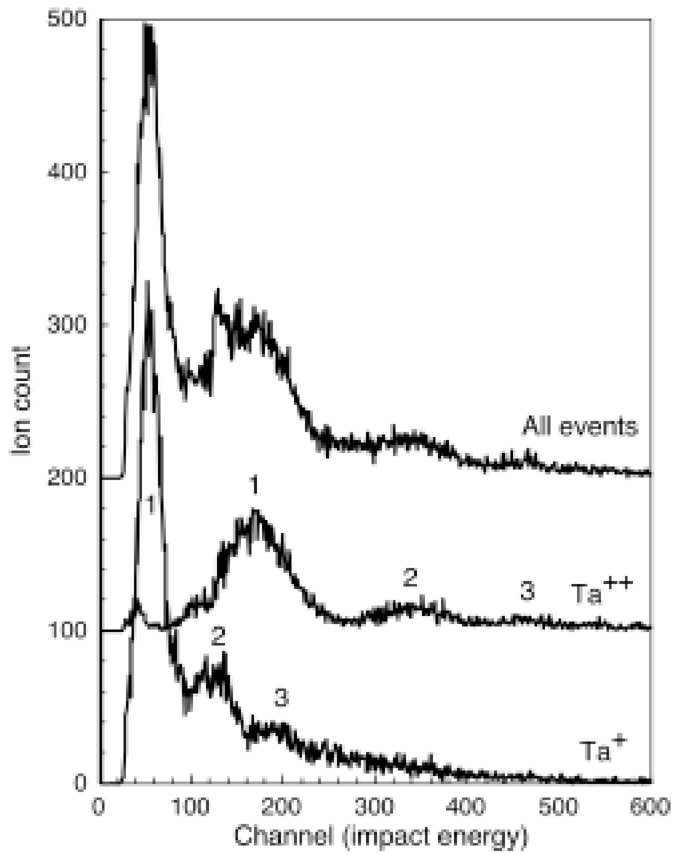

Fig. 4. Impact energy spectra for all events, Ta^{++}, and Ta^{+} with different time-gates in the STJ detector with the 70nm-thick Al layers. Multi-hit events are indicated by the numbers.

As mentioned above, the detector with the 70nm-thick Al layers has a better spatial uniformity than the detector with the 50nm-thick Al layers. Therefore, we expected the better discrimination of the ionic states and multi-hit events. However, it was opposite, as shown in Fig. 4. In the Ta^+ spectrum, distinguishable three peaks are observed in a range less than 240 ch., and are assigned to the single, double, and triple hit events of the Ta^+ ions. The peak separation is not as good as in Fig.3. The Ta^{++} single hit events appearing near 170cn. have the deposited energy higher than those of the Ta^+ double hit events, as is observed in Fig. 3. Comparison between the single Ta^+ peak and the single Ta^{++} peak is also the same as in Fig. 3.

One of the possible reasons for this unexpected result is that the detector temperature is as high as 1.3K. The density of the thermally excited quasiparticles in the 70nm-thick Al layers is higher than that in the 50nm-thick Al layers. Therefore, it is expected the detector output pulses are lowered, and proper detector operation is difficult.

IV. Conclusion

The performance of the STJ detectors for time-of-flight mass spectroscopy has been examined by using the Ta cluster ion source, which produces the peaks with a mass interval of 180.95 Da in the mass spectra. The clusters containing less than about twenty Ta atoms appear as the distinct peaks. The impact energy spectra exhibit the non-linear peak positions for the single-hit and the multi-hit events of the Ta^+ and Ta^{++} ions. It is suggested that the secondary particle emission, which reduces the deposited energy fraction, is responsible for the abnormal nonlinearity. There is room for the discussion about the energy transfer mechanism of the kinetic energy to the superconducting electrodes.

The STJ detector having a better spatial uniformity for 6keV x-rays unexpectedly exhibits the poor ionic state and multi-hit discrimination. One possible reason is the high operating temperature of the junction detectors because of the heat radiation from room temperature. We plan to reduce heat radiation.

Acknowledgment

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